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**(54) Title:** LIQUID DETERGENT COMPOSITIONS**(57) Abstract**

Liquid detergent compositions, particularly to dishwashing compositions comprising high levels of nonionic surfactants and suds enhancing polymers having the formula Cap-E<sub>n</sub>-B-E<sub>n</sub>-Cap.

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## LIQUID DETERGENT COMPOSITIONS

TECHNICAL FIELD OF THE INVENTION

The present invention relates to liquid detergent compositions, particularly to dishwashing compositions comprising high levels of nonionic surfactants and suds enhancing polymers.

BACKGROUND OF THE INVENTION

The types of soils commonly encountered in a dishwashing load are often, although not exclusively derived from food. Non food derived soils which are often found include, for example lipstick and nicotine. The soils which are the hardest to remove are usually greasy soils. Particularly difficult soils to remove are those which have been baked-on or burnt-on or soils which have been allowed to harden onto the dish article.

Nonionic surfactants are widely used in detergent compositions. However, except for selected nonionic surfactants, the art teaches their use generally is limited to lower levels in certain polymer-containing compositions. For example, U.S. Patent 5,167,872, issued December 1, 1992 to Pancheri et al., states: "However, when the level of anionic surfactant is less than about 20%, the compositions should not contain any substantial amount of conventional nonionic surfactant, e.g., an alkylpolyethoxylate, in addition to the polymeric surfactant. Large amounts of conventional nonionic surfactants, e.g., more than about three or four percent, tend to harm the sudsing ability of the compositions." (At column 8, lines 25-32.)

Example XXIII therein (beginning at column 19, line 48) provides grease control results for a composition containing a preferred polymer useful in the present invention (designated therein as compound U). However, this composition does not contain any nonionic surfactant, consistent with the hereinbefore noted teachings of this document. Surprisingly, the present invention has discovered that selected polymers of this type provide enhanced sudsing for these liquid dishwashing compositions, even when higher than 3% nonionic surfactants are present.

It is therefore an object of the present invention to provide liquid dishwashing detergent compositions comprising selected polymers and higher levels of nonionic surfactants which have good cleaning and sudsing properties. These and other objects of the present invention are apparent from the detailed description provided hereinafter.

BACKGROUND ART

As noted hereinbefore, U.S. Patent 5,167,872, issued December 1, 1992 to Pancheri et al., relates to compositions containing low levels of nonionic. See also: U.S. Patent 4,904,359, issued February 27, 1990 to Pancheri et al.

Disclosures relating to polyhydroxy fatty acid amides include: U.S. Patent 5,332,528, to Pan et al. issued July 26, 1994; U.S. 5,288,431, to Huber et al. issued February 22, 1994; U.S. Patent 5,378,409, to Ofosu-Asante issued January 3, 1995; U.S. Patent 5,376,310, to Cripe et al. issued December 27, 1994; U.S. Patent 5,269,974, to Ofosu-Asante issued December 14, 1993; U.S. Patent 5,417,893, to Ofosu-Asante issued May 23, 1995; European Patent Publication # 550,652 by Fu et al.; European Patent Publication # 551,410 by Rolfe; European Patent Publication # 550,653 by Mao; European Patent Publication # 550,606 by Collins; European Patent Publication # 602,179 by Ofosu-Asante et al.; and WO Publication #94/12608, by Vinson;

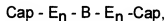
Disclosures relating to polymers include: U.S. Patent 4,968,451, issued November 6, 1990 to Scheibel et al.; and U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

SUMMARY OF THE INVENTION

The present invention is a liquid detergent composition comprising:

(a) greater than about 3% nonionic surfactants selected from alkylpolysaccharides, polyhydroxy fatty acid amides, alkyl polyethoxylates, alkyl phenol ethoxylates and mixtures thereof; and

(b) at least about 0.1% of a suds enhancing polymer having the formula:



wherein each Cap is independently selected from the group consisting of  $-\text{CH}_2\text{CH}(\text{SO}_2^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}(\text{SO}_3^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}_3$ , and  $-\text{CH}_3$ ;

at least one of the  $\text{E}_n$  is a poly(oxyethylene)oxy moiety having the formula  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_{n-1} - \text{CH}_2\text{CH}_2\text{O}-$ , wherein n is from about 7 to about 43; and

B is a polymer backbone of the formula  $(\text{T-S})_m\text{-T}$  wherein: T is a terephthaloyl moiety having the formula  $-\text{C}(\text{O})-(\text{C}_6\text{H}_4)-\text{C}(\text{O})-$ ; each S is independently selected from oxypropyleneoxy ("PG") moieties having the

formulas  $-\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}-$  or  $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}-$  and oxyethyleneoxy ("EG") moieties having the formula  $-\text{OCH}_2\text{CH}_2\text{O}-$ ; m is within the range of from about 0 to about 7; and the ratio of EG:PG is less than about 3:1, preferably less than about 1:1.

All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is a liquid detergent composition comprising one or more nonionic surfactants and selected suds enhancing polymers.

##### Nonionic Surfactants:

According to the present invention the detergent composition comprises as an essential feature at least about 3%, more preferably at least about 4%, and most preferably at least about 5% of nonionic surfactant selected from alkylpolysaccharides, polyhydroxy fatty acid amides, alkyl polyethoxylates, alkyl phenol ethoxylates and mixtures thereof. Preferably said nonionic surfactant is selected from polyhydroxy fatty acid amides, alkyl polyethoxylates, and mixtures thereof. Preferred levels are from about 3% to about 50%, more preferably from about 3% to about 30%, and most preferably from about 4% to about 20%.

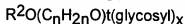
According to the present invention suitable alkylpolysaccharides for use herein are nonionic alkylpolysaccharides. Alkylpolysaccharides suitable for use herein are disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 11 to about 30, more preferably 11 to 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.0 to about 10, preferably from about 1.0 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.)

The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units. Optionally, and less desirably, there can be a

polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight-chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxyl groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta- and hexagluco-sides.

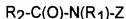
The preferred alkylpolyglycosides have the formula:



wherein R<sup>2</sup> is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 0 to 3 preferably 2 to 3, t is from 0 to 10, preferably 0, x is from 1.0 to 10, preferably from 1.0 to 3, most preferably from 1.3 to 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

According to the present invention the dishwashing compositions preferably comprise from about 0% to about 50%, more preferably from about 0.1% to about 30%, most preferably from about 0.5% to about 5% of said alkylpolysaccharide surfactant.

According to the present invention suitable polyhydroxy fatty acid amides for use herein are according to the formula

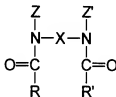


wherein R<sub>1</sub> is H, a C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or mixtures thereof, preferably a C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably a C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably a C<sub>1</sub>, and R<sub>2</sub> is a C<sub>5</sub>-C<sub>31</sub> hydrocarbyl, preferably straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, most preferably straight chain C<sub>11</sub>-C<sub>17</sub> alkyl

or alkenyl or mixtures thereof; and Z is a polyhydrocarbonyl having a linear hydrocarbonyl chain with at least 3 hydroxyl groups directly connected to the chain or an alkoxyated derivative thereof. Z is preferably derived from a reducing sugar in reductive amination reaction; more preferably Z is a glycidyl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials high dextrose corn syrup, high fructose corn syrup and high maltose corn syrup can be utilised as well as individual sugars listed above. It should be understood that these corn syrups may yield a mixture of sugar components for Z. Z is preferably selected from the group consisting of  $-\text{CH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_n-1-\text{CH}_2\text{OH}$ , or  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$  and alkoxyated derivatives thereof, wherein n is an integer from 3 to 5 inclusive and R' is hydrogen or a cyclic or aliphatic monosaccharide. Most preferred are the glycidyls wherein n is 4, particularly  $\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ .

According to the formula R<sub>1</sub> can be for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R<sub>5</sub>-CO-N< can be for example cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, talloamide etc. Z can be 1-deoxyglycidyl, 2-deoxyfructidyl, 1-deoxymaltidyl, 1-deoxylactidyl, 1-deoxygalactidyl, 1-deoxymannidyl, 1-deoxymaltotriidyl, etc.

Other polyhydroxy fatty acid amides suitable for use herein are gemini polyhydroxy fatty acid amides having the formula:



wherein: X is a bridging group having from about 2 to about 200 atoms; Z and Z' are the same or different alcohol-containing moieties having two or more hydroxyl groups (e.g., glycerol, and units derived from reducing sugars such as glucose, maltose and the like), or either one (but not both) of Z or Z' is hydrogen; and R and R' are the same or different hydrocarbonyl moieties having from about 1 to about 21 carbon atoms and can be saturated, branched or unsaturated (e.g., oleoyl) and mixtures thereof.

Preferred X groups are selected from substituted or unsubstituted, branched or linear alkyl, ether alkyl, amino alkyl, or amido alkyl moieties having from about 2 to about 15 carbon atoms. Preferred alkyl moieties are unsubstituted, linear alkyl moieties having the formula  $-(CH_2)_n-$ , wherein n is an integer from 2 to about 15, preferably from 2 to about 10, and most preferably from 2 to about 6; and also unsubstituted, branched alkyl moieties having from 3 to about 15 carbon atoms, preferably from 3 to about 10 carbon atoms, and most preferably from 3 to about 6 carbon atoms. Most preferred are ethylene and propylene (branched or linear) alkyl moieties. Also preferred are unsubstituted, branched or linear ether alkyl moieties having the formula  $-R^2-(O-R^2)_m-$ , wherein each  $R^2$  is independently selected from C<sub>2</sub>-C<sub>8</sub> branched or linear alkyl and/or aryl moieties (preferably ethyl, propyl or combinations thereof) and m is an integer from 1 to about 5. X may also be unsubstituted, branched or linear amino and/or amido alkyl moieties having the formula  $-R^2-(N(R^3)-R^2)_m-$ , wherein each  $R^2$  is independently selected from C<sub>2</sub>-C<sub>8</sub> branched or linear alkyl and/or aryl moieties (preferably ethyl, propyl or combinations thereof), m is an integer from 1 to about 5, and  $R^3$  is selected from hydrogen, C<sub>1</sub>-C<sub>5</sub> alkyl, and  $-C(O)R^4-$ , wherein  $R^4$  is C<sub>1</sub>-C<sub>21</sub> alkyl, including  $-C(O)R$ . The X moiety may be derived from commercially available amine compounds such as, for example, Jeffamines<sup>R</sup> (supplied by Texaco) such as JED600, JEDR148, JEDR192, JED230, JED2000, J-D230 and J-D400.

Preferred X moieties therefore include:  $-(CH_2)_2-$ ,  $-(CH_2)_3-$ ,  $-(CH_2)_4-$ ,  $-(CH_2)_5-$ ,  $-(CH_2)_6-$ ,  $-CH_2CH(CH_3)(CH_2)_3-$ ,  $-(CH_2)_2-O-(CH_2)_2-$ ,  $-(CH_2)_3-O-(CH_2)_3-$ ,  $-(CH_2)_2-O-(CH_2)_3-$ ,  $-(CH_2)_2-O-(CH_2)_2-O-(CH_2)_2-$ ,  $-(CH_2)_3-O-(CH_2)_2-O-(CH_2)_3-$ ,  $-(CH_2)_2-O-(CH_2)_3-O-(CH_2)_2-$ ,  $-(CH_2)_2-NH-(CH_2)_2-$ ,  $-(CH_2)_3-NH-(CH_2)_3-$ ,  $-(CH_2)_2-NH-(CH_2)_3-$ ,  $-(CH_2)_2-N(C(O)R)-(CH_2)_2-$ ,  $-(CH_2)_3-N(C(O)R)-(CH_2)_3-$ ,  $-(CH_2)_2-NH(C_6H_4)NH-(CH_2)_2-$ ,  $-(CH_2)_3-NH(C_6H_4)NH-(CH_2)_3-$ ,  $-(CH_2)_2-NHCH_2(C_6H_4)CH_2NH-(CH_2)_2-$ ,  $-(CH_2)_3-NHCH_2(C_6H_4)CH_2NH-(CH_2)_3-$ , etc.

Preferred Z and Z' groups are independently selected from polyhydroxyhydrocarbonyl moieties having a linear hydrocarbonyl chain with at least 2 hydroxyls (in the case of glycerol) or at least 3 hydroxyls (in the case of other sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z and Z' preferably will be derived from a reducing sugar, more preferably Z and/or Z' is a glycidyl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose,

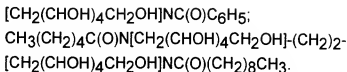


galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z and Z'. It should be understood that it is by no means intended to exclude other suitable raw materials. Z and/or Z' preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_p-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{p-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}^1)(\text{CHOH})-\text{CH}_2\text{OH}$ , where p is an integer from 1 to 5, inclusive, and R<sup>1</sup> is H or a cyclic mono- or polysaccharide, and alkoxyalted derivatives thereof. Most preferred are glycityls wherein p is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$ .

Preferred R and R' groups are independently selected from C<sub>3</sub>-C<sub>21</sub> hydrocarbyl moieties, preferably straight or branched chain C<sub>3</sub>-C<sub>13</sub> alkyl or alkenyl, more preferably straight chain C<sub>5</sub>-C<sub>11</sub> alkyl or alkenyl, most preferably straight chain C<sub>5</sub>-C<sub>9</sub> alkyl or alkenyl, or mixtures thereof. R-CO-N< and/or R'-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Examples of such compounds therefore include, but are not limited to:

$\text{CH}_3(\text{CH}_2)_6\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_6\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_8\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_8\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_{10}\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_{10}\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_8\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_8\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_8\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_3-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_8\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_8\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_8\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{CH}_3)\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_6\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_6\text{CH}_3;$   
 $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-$   
 $[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC}(\text{O})(\text{CH}_2)_8\text{CH}_3;$   
 $\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_3-\text{O}-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-$



These compounds can be readily synthesized from the following disugar diamines:

$$\begin{aligned} &\text{HN}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2- \\ &[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NH}; \quad \text{HN}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-\text{CH}_2\text{CH}(\text{CH}_3)(\text{CH}_2)_3- \\ &[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NH}; \quad \text{HN}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}- \\ &(\text{CH}_2)_2-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NH}; \quad \text{HN}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]-(\text{CH}_2)_3-\text{O}- \\ &(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_3-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NH}; \text{ and } \text{HN}[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]- \\ &(\text{CH}_2)_3-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NH}. \end{aligned}$$

The compositions according to the present invention comprise from about 0% to about 50% , preferably from about 1% to about 20%, most preferably from about 2% to about 10%, of said poly hydroxy fatty acid amide.

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols (herein referred to as "alkyl phenol ethoxylates") are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide.

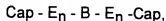
The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein (herein referred to as "alkyl polyethoxylates"). The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Most preferred are the condensation products of alcohols having an alkyl group containing from 8 to 14 carbon atoms with from about 6 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C<sub>11</sub>-C<sub>15</sub> linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C<sub>12</sub>-C<sub>14</sub> primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 9

moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 6.54 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C<sub>14</sub>-C<sub>15</sub> linear alcohol with 4 moles of ethylene oxide), Neodol™ 23-3 (the condensation product of C<sub>12</sub>-C<sub>13</sub> linear alcohol with 3 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro™ EOBN (the condensation product of C<sub>13</sub>-C<sub>15</sub> alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, Dobanol 91 marketed by the Shell Chemical Company and Lial 123 marketed by Enichem.

The compositions according to the present invention comprise in total from about 0% to about 50% , preferably from about 0.5% to about 10%, most preferably from about 1% to about 5%, of said alkyl phenol ethoxylates, alkyl polyethoxylates, or mixtures thereof.

#### Suds Enhancing Polymers:

According to the present invention the detergent composition also comprises as an essential feature at least about 0.1%, more preferably at least about 0.5%, and most preferably at least about 1% of one or more suds enhancing polymers having the formula:

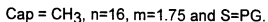


wherein each Cap is independently selected from the group consisting of  $-\text{CH}_2\text{CH}(\text{SO}_2^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}(\text{SO}_3^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}_3$ , and  $-\text{CH}_3$ ;

at least one of the  $\text{E}_n$  is a poly(oxyethylene)oxy moiety having the formula  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_{n-1} - \text{CH}_2\text{CH}_2\text{O}-$ , wherein n is from about 7 to about 43; and

B is a polymer backbone of the formula  $(\text{T-S})_m\text{-T}$  wherein: T is a terephthaloyl moiety having the formula  $-\text{C}(\text{O})-(\text{C}_6\text{H}_4)-\text{C}(\text{O})-$ ; each S is independently selected from oxypropyleneoxy ("PG") moieties having the formulas  $-\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}-$  or  $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}-$  and oxyethyleneoxy ("EG") moieties having the formula  $-\text{OCH}_2\text{CH}_2\text{O}-$ ; m is within the range of from about 0 to about 7; and the ratio of EG:PG is less than about 3:1, preferably less than about 1:1.

A preferred polymer for use herein has the formula hereinbefore wherein:



Preferred levels of polymer are from about 0.1% to about 5%, more preferably from about 0.2% to about 3%, and most preferably from about 0.5% to about 2%.

Methods for making such polymers are known in the art, being described for example in U.S. Patent 4,968,451, issued November 6, 1990 to Scheibel et al., and U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

According to the broadest aspect of the present invention the detergent composition may comprise a number of optional ingredients such as additional surfactants, builders, chelants, soil release agents, anti-redeposition agents, polymeric dispersing agents, bleaches, enzymes, calcium and magnesium ions, brightener, perfumes and dyes.

Optional Surfactants:

Suitable optional surfactants for use herein include other anionic, nonionic, cationic, amphoteric and zwitterionic surfactants and mixtures thereof.

Anionic surfactant

Anionic surfactants suitable for use herein may be essentially any anionic surfactant, including anionic sulphate or carboxylate surfactant.

Alkyl or hydroxyalkyl alkoxyated sulphates:

According to the present invention suitable alkyl or hydroxyalkyl alkoxyated sulphates for use herein are of the formula  $RO(A)_mSO_3M$ , wherein R is an unsubstituted  $C_{11}$ - $C_{24}$  alkyl or hydroxyalkyl component, preferably a  $C_{12}$ - $C_{20}$  alkyl or hydroxyalkyl, more preferably a  $C_{12}$ - $C_{18}$  alkyl or hydroxyalkyl component, A is an ethoxy or propoxy group, m is from 1 to 15, more preferably from 1 to 10, and M is H or a cation which may be selected from metal cations such as sodium, potassium, lithium, calcium, magnesium, ammonium or substituted ammonium. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations such as tetramethyl-ammonium, dimethyl piperidium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine and triethanolamine and mixtures thereof. Exemplary surfactants are  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (2.25) sulphate,  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (3) sulphate and  $C_{12}$ - $C_{18}$  alkyl polyethoxylate (4) sulphate wherein M is selected from sodium or potassium.

C<sub>12</sub>-C<sub>14</sub> alkyl sulphate which has been ethoxylated with an average of from 0.5 to 4 moles of ethylene oxide per molecule is especially preferred.

According to the present invention the compositions may comprise from about 5% to about 50%, preferably from about 5% to about 35%, most preferably from about 10% to about 25% of said alkyl alkoxyated sulphate.

#### Sulphonates:

As used herein the term deterative sulphonates refers to the salts (e.g. alkali metal and ammonium salts) of C<sub>11</sub>-C<sub>24</sub>, preferably C<sub>12</sub>-C<sub>20</sub> linear alkylaryl sulphonates, particularly linear alkyl benzene sulphonates, primary or secondary alkane sulphonates, alkene sulphonates such as  $\alpha$ -olefin sulphonates, ether sulphonates, sulphonated polycarboxylic acids, oxyalkane sulphonates (fatty acid isethionates), acylamino alkane sulphonates (taurides), alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphonates, and any mixtures thereof. Preferred alkyl sulphonates for use herein are C<sub>12</sub>-C<sub>18</sub>, sodium paraffin sulphonates and C<sub>12</sub>-C<sub>18</sub> linear alkyl benzene sulphonates.

According to the present invention the detergent composition may comprise from about 5% to about 50%, preferably from about 10% to about 25% of said deterative sulphonate.

#### Anionic sulphate surfactant

The anionic sulphate surfactant may be any organic sulphate surfactant. The counterion for the anionic sulphate surfactant component is preferably selected from calcium, sodium, potassium, magnesium, ammonium, or alkanol-ammonium, and mixtures thereof, with calcium and magnesium being preferred for cleaning and sudsing, respectively.

Other suitable anionic surfactants for use herein include C<sub>9</sub>-C<sub>17</sub> acyl-N-(C<sub>1</sub>-C<sub>4</sub> alkyl) glucamine sulphate.

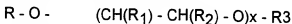
#### Anionic alkyl ethoxy carboxylate surfactant

Alkyl ethoxy carboxylates suitable for use herein include those with the formula  $RO(CH_2CH_2O)_xCH_2COO-M^+$  wherein R is a C<sub>12</sub> to C<sub>16</sub> alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20%, preferably less than 15%, most preferably less than 10%, and the amount of material where x is greater than 7, is less than 25%, preferably less than 15%, most preferably less than 10%, the average x is from 2 to 4 when the average R is C<sub>13</sub> or less, and the average x is from 3 to 6 when the average R is greater than C<sub>13</sub>, and M is a cation, preferably chosen from alkali

metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C<sub>12</sub> to C<sub>14</sub> alkyl group.

Anionic alkyl polyethoxy polycarboxylate surfactant

Alkyl polyethoxy polycarboxylate surfactants suitable for use herein include those having the formula:



wherein R is a C<sub>6</sub> to C<sub>18</sub> alkyl group, x is from 1 to 25, R<sub>1</sub> and R<sub>2</sub> are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R<sub>1</sub> or R<sub>2</sub> is a succinic acid radical or hydroxysuccinic acid radical, and R<sub>3</sub> is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

Secondary soap surfactants (aka "alkyl carboxyl surfactants") useful herein are those which contain a carboxyl unit connected to a secondary carbon. It is to be understood herein that the secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should contain no ether linkages, no ester linkages and no hydroxyl groups. There should be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 10-16 total carbon atoms, as is described for example in PCT application WO 94/12608, published June 9, 1994 by The Procter & Gamble Company.

The following general structures further illustrate some of the secondary soap surfactants (or their precursor acids) useful herein.

A. A highly preferred class of secondary soaps useful herein comprises the secondary carboxyl materials of the formula R<sup>3</sup> CH(R<sup>4</sup>)COOM, wherein R<sup>3</sup> is CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub> and R<sup>4</sup> is CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>, wherein y can be 0 or an integer from 1 to 6, x is an integer from 6 to 12 and the sum of (x + y) is 6-12, preferably 7-11, most preferably 8-9.

B. Another class of secondary soaps useful herein comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R<sup>5</sup>-R<sup>6</sup>-COOM, wherein R<sup>5</sup> is C<sup>7</sup>-C<sup>10</sup>, preferably C<sup>8</sup>-C<sup>9</sup>, alkyl or alkenyl and R<sup>6</sup> is a ring structure, such as

benzene, cyclopentane and cyclohexane. (Note: R<sup>5</sup> can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another class of secondary soaps comprises secondary carboxyl compounds of the formula  $\text{CH}_3(\text{CHR})_k(\text{CH}_2)_m(\text{CHR})_n\text{-CH}(\text{COOM})(\text{CHR})_o(\text{CH}_2)_p(\text{CHR})_q\text{-CH}_3$ , wherein each R is C<sub>1</sub>-C<sub>4</sub> alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion, e.g., H, alkali metal, alkaline earth metal, ammonium, alkanolammonium, di- and tri-alkanolammonium, and C<sub>1</sub>-C<sub>5</sub> alkyl substituted ammonium. Sodium is convenient, as is diethanolammonium.

Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid, 2-pentyl-1-heptanoic acid and isopentadecanoic acid.

#### Other anionic surfactants

Other anionic surfactants useful for deterative purposes can also be included in the compositions hereof. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, fatty oleyl glycerol sulphates, alkyl phenol ethylene oxide ether sulphates, alkyl phosphates, alkyl succinates and sulphosuccinates, monoesters of sulphosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulphosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), N-acyl C<sub>6</sub>-20 sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

Compositions according to the present invention may comprise at least about 3%, preferably from about 3% to about 40%, most preferably from about 3% to about 30% of said anionic surfactants.

#### Nonionic surfactant

Suitable additional optional nonionic detergent surfactants for use herein include the following. According to the present invention the

compositions may comprise from about 0% to about 30%, preferably from about 0.1% to about 25%, more preferably from about 0.5% to about 20% of said optional nonionic surfactants.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. Examples of compounds of this type include certain of the commercially-available Pluronic<sup>TM</sup> surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

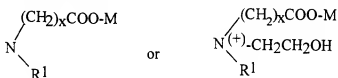
The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic<sup>TM</sup> compounds, marketed by BASF.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the alkyl amphocarboxylic acids of the formula:



wherein R is a C<sub>8</sub>-C<sub>18</sub> alkyl group, and R<sub>i</sub> is of the general formula:



wherein R<sup>1</sup> is a (CH<sub>2</sub>)<sub>x</sub>COOM or CH<sub>2</sub>CH<sub>2</sub>OH, and x is 1 or 2 and M is preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred R alkyl chain length is a C<sub>10</sub> to C<sub>14</sub> alkyl group. A preferred amphocarboxylic acid is produced from fatty imidazolines wherein the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid. A suitable example of an alkyl amphodicarboxylic acid for use herein is the amphoteric surfactant Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.



Amine oxide surfactant

Preferred for use in the present invention compositions are amine oxides, individually or as amine oxide mixtures comprising a first amine oxide according to the formula  $R_1R_2R_3N-O$ , wherein  $R_1$  and  $R_2$  are independently  $C_1$ - $C_3$  alkyl or hydroxy alkyl groups and  $R_3$  is an hydrocarbly group having an average carbon chain length of  $C_7$ - $C_9$ . Said first amine oxide is in combination with a second amine oxide according to the formula  $R_4R_5R_6N-O$  wherein  $R_4$  and  $R_5$  are independently  $C_1$ - $C_3$  alkyl or hydroxyalkyl groups and  $R_6$  is a  $C_{12}$ - $C_{14}$  hydrocarbly group and mixtures thereof. Preferably  $R_1$ ,  $R_2$ ,  $R_4$  and  $R_5$  are methyl groups.  $R_3$  is preferably an alkyl group with an average carbon chain length of 8. More preferably  $R_3$  is a linear  $C_8$  alkyl group, although it may exhibit a degree of branching. Preferably the ratio of said first amine oxide to said second amine oxide is from 100:1 to 1:100 more preferably from 50:1 to 1:50, most preferably from 10:1 to 1:10.

The present invention preferably comprises from about 0% to about 20%, preferably from about 0.5% to about 15%, more preferably from about 1% to about 15% of an amine oxide or mixture of amine oxides. Preferably an amine oxide mixture comprises from about 1% to about 99%, more preferably from about 5% to about 90% of said first amine oxide.

In addition to  $C_7$ -9 and  $C_{12}$ -14 amine oxide ingredients, other amine oxides useful as amphoteric surfactants may be used herein. Such optional but highly preferred amine oxides suitable for use have the formula:



wherein  $R_7$  is selected from an alkyl, hydroxyalkyl, acylamidopropyl and alkyl phenyl group, or mixtures thereof, containing from 10 to 20 carbon atoms, preferably 10 to 14 carbon atoms; and  $R_8$  and  $R_9$  are independently  $C_1$ -3 alkyl or  $C_2$ -3 hydroxyalkyl groups, or a polyethylene oxide group containing from 1 to 3, preferably 1, ethylene oxide groups. These amine oxide surfactants in particular include  $C_{10}$ - $C_{14}$  alkyl dimethyl amine oxides and  $C_{10}$ - $C_{12}$  alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include diethyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide and dodecylamidopropyl dimethylamine oxide.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions herein.

Betaine surfactant

According to the present invention the compositions may thus comprise betaines. The betaines useful, as zwitterionic surfactants, in the present invention are those compounds having the formula  $R(R^1)_2N^+R^2COO^-$  wherein R is a C<sub>6</sub>-C<sub>18</sub> hydrocarbyl group, preferably a C<sub>10</sub>-C<sub>16</sub> alkyl group or C<sub>10</sub>-16 acylamido alkyl group, each R<sup>1</sup> is typically C<sub>1</sub>-C<sub>3</sub> alkyl, preferably methyl, and R<sup>2</sup> is a C<sub>1</sub>-C<sub>5</sub> hydrocarbyl group, preferably a C<sub>1</sub>-C<sub>3</sub> alkylene group, more preferably a C<sub>1</sub>-C<sub>2</sub> alkylene group. Examples of suitable betaines include coconut acylamidopropyl dimethyl betaine; hexadecyl dimethyl betaine; C<sub>12</sub>-14 acylamidopropyl betaine; C<sub>8</sub>-14 acylamido hexyldiethyl betaine; 4-[C<sub>14</sub>-16 acylmethylamidodiethylammonio]-1-carboxybutane; C<sub>16</sub>-18 acylamidodimethyl betaine; C<sub>12</sub>-16 acylamidopentanedithyl betaine; C<sub>12</sub>-16 acylmethylamidodimethyl betaine. Preferred betaines are C<sub>12</sub>-18 dimethyl-ammonio hexanoate and the C<sub>10</sub>-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines.

The complex betaines suitable for use herein have the formula:



wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, preferably 12 to 14 carbon atoms, A is the group (C(O)), n is 0 or 1, R<sub>1</sub> is hydrogen or a lower alkyl group, x is 2 or 3, y is an integer of 0 to 4, Q is the group -R<sub>2</sub>COOM wherein R<sub>2</sub> is an alkylene group having from 1 to 6 carbon atoms and M is hydrogen or an ion from the groups alkali metals, alkaline earth metals, ammonium and substituted ammonium and B is hydrogen or a group Q as defined.

According to the present invention the composition may comprise from 0% to 10%, preferably from 0% to 5% of said betaines.

Sultaines

The sultaines useful in the present invention are those compounds having the formula  $(R(R^1)_2N^+R^2SO_3^-)$  wherein R is a C<sub>6</sub>-C<sub>18</sub> hydrocarbyl group, preferably a C<sub>10</sub>-C<sub>16</sub> alkyl group, more preferably a C<sub>12</sub>-C<sub>13</sub> alkyl group, each R<sup>1</sup> is typically C<sub>1</sub>-C<sub>3</sub> alkyl, preferably methyl, and R<sup>2</sup> is a C<sub>1</sub>-C<sub>6</sub> hydrocarbyl group, preferably a C<sub>1</sub>-C<sub>3</sub> alkylene or, preferably, hydroxyalkylene group.

The zwitterionics herein above may also be present in small quantities so as to deliver further suds enhancing benefits to the compositions.

#### Enzymes

Compositions according to the present invention may additionally comprise enzymes. Suitable enzymes for use herein include lipolytic enzymes, proteolytic enzymes and amylolytic enzymes. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes* described for example in EP-B-0218272. Preferred commercially available proteolytic enzymes include Alcalase and Savinase (Novo Industries A/S) and Maxatase (International Bio-Synthetics, Inc.) Preferred amylases include for example alpha-amylases obtained from a special strain of *B licheniformis*, described for example in GB 1 269 839. Preferred commercially available amylases include Termamyl (Novo Industries A/S). The compositions according to the present invention may comprise from 0.001% to 1% , more preferably from 0.01% to 0.1% of active enzyme. In addition the composition may comprise an enzyme stabilising system.

Liquid dishwashing compositions according to the present invention may comprise any of the ingredients listed herein above. In addition the dishwashing compositions may comprise other ingredients such as bleaches, bactericides, anti-tarnish agents, chelants, suds enhancers, opacifiers, solvents, hydrotropes, calcium and magnesium ions and perfumes and dyes.

#### Hydrotropes

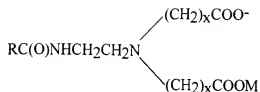
A hydrotrope is typically added to the compositions of the present invention, and may be present at levels of from 0% to 40%, preferably from 1% to 15%, by weight.

Useful hydrotropes include sodium, potassium, calcium and ammonium salts of xylene sulphonates, toluene sulphonate and cumene sulphonate and mixtures thereof. Other compounds useful as hydrotropes herein include polycarboxylates and urea. Some polycarboxylates have calcium chelating properties as well as hydrotropic properties.

An example of a commercially available alkylpolyethoxy polycarboxylate which can be employed herein is POLY-TERGENT C™, Olin Corporation, Cheshire, CT.

Another compound useful as a hydrotrope is alkyl amphodicarboxylic acid of the generic formula:

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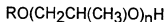


wherein R is a C<sub>8</sub> to C<sub>18</sub> alkyl group, x is from 1 to 2, M is preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium, and mixtures thereof with magnesium ions. The preferred alkyl chain length (R) is a C<sub>10</sub> to C<sub>14</sub> alkyl group and the dicarboxylic acid functionally is diacetic acid and/or dipropionic acid.

A suitable example of an alkyl amphodicarboxylic acid is the amphoteric surfactant Miranol R™ 2CM Conc. manufactured by Miranol, Inc., Dayton, NJ.

#### Organic solvent

The compositions of the invention will most preferably contain an organic solvent system present at levels of from about 1% to about 30% by weight, preferably from about 1% to about 20% by weight, more preferably from about 2% to about 15% by weight of the composition. The organic solvent system may be a mono, or mixed solvent system; but is preferably in mixed solvent system. Preferably, at least the major component of the solvent system is of low volatility. Suitable organic solvents for use herein has the general formula:



wherein R is an alkyl, alkenyl, or alkyl aryl group having from 1 to 8 carbon atoms, and n is an integer from 1 to 4. Preferably, R is an alkyl group containing 1 to 4 carbon atoms, and n is 1 or 2. Especially preferred R groups are n-butyl or isobutyl. Preferred solvents of this type are 1-n-butoxypropane-2-ol (n=1); and 1(2-n-butoxy-1-methylethoxy)propane-2-ol (n=2), and mixtures thereof.

Other solvents useful herein include the water soluble CARBITOL or CELLOSOLVE solvents. These solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl.

Other suitable solvents are benzyl alcohol, and diols such as 2-ethyl-1,3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol. The low molecular weight, water-soluble, liquid polyethylene glycols are also suitable solvents for use herein.

The alkane mono and diols, especially the C<sub>1</sub>-C<sub>6</sub> alkane mono and diols are suitable for use herein. C<sub>1</sub>-C<sub>4</sub> monohydric alcohols (eg: ethanol, propanol, isopropanol, butanol and mixtures thereof) are preferred, with ethanol particularly preferred. The C<sub>1</sub>-C<sub>4</sub> dihydric alcohols, including propylene glycol, are also preferred.

#### Thickening agents

The compositions according to the present invention may additionally comprise thickening agents, such as polyquaternium cellulose cationic polymer, for example Quatrisoft<sup>®</sup> available from the Amerchol Corporation.

#### Calcium

Compositions according to the present invention may optionally comprise from about 0.01% to about 3%, more preferably from about 0.15% to about 0.9% of calcium ions. It has been found that the presence of calcium greatly improves the cleaning of greasy soils for compositions containing polyhydroxy fatty acid amide. This is especially true when the compositions are used in softened water, which contains few divalent ions.

The calcium ions can, for example, be added as a chloride, hydroxide, oxide, formate or acetate, xylene sulphonate, or nitrate salt. If the anionic surfactants are in the acid form, the calcium can be added as a calcium oxide or calcium hydroxide slurry in water to neutralise the acid.

The calcium ions may be present in the compositions as salts. The amount of calcium ions present in compositions of the invention may be dependent upon the amount of total anionic surfactant present herein. The molar ratio of calcium ions to total anionic surfactant is preferably from 1:0.1 to 1:25 more preferably from 1:2 to 1:10, for compositions of the invention.

#### Calcium stabilising agent

In order to provide good product stability, and in particular to prevent the precipitation of insoluble calcium salts malic, maleic or acetic acid, or their salts, or certain lime soap dispersant compounds may be added to the composition of the present invention comprising calcium. Where calcium is present, malic, maleic or acetic acid, or their salts can be added at levels of from 0.05% to 10% of the composition and a molar ratio with calcium of from 10:1 to 1:10.

### Magnesium

From 0.01% to 3%, most preferably from 0.15% to 2%, by weight, of magnesium ions are preferably added to the liquid detergent compositions of the invention for improved product stability, as well as improved sudsing.

If the anionic surfactants are in the acid form, then the magnesium can be added by neutralisation of the acid with a magnesium oxide or magnesium hydroxide slurry in water. Calcium can be treated similarly. This technique minimises the addition of chloride ions, which reduces corrosive properties. The neutralized surfactant salts and the hydrotrope are then added to the final mixing tank and any optional ingredients are added before adjusting the pH.

### pH of the compositions

The compositions according to the present invention formulated for use in manual dishwashing applications are preferably formulated to have a pH at 20°C of from about 3 to about 12, preferably from about 6 to about 9, most preferably from about 6.5 to about 8.5.

In another aspect of the present invention the composition may be formulated for use as in pre-treatment applications whereby the composition is applied in essentially the concentrated form onto the dishes. Preferably the composition is allowed to remain on the dishes for a period of time. Compositions for use in such applications preferably have a pH of from about 3 to about 14, more preferably from about 3 to about 5 or greater than about 8.

### Liquid compositions

According to the present invention the detergent compositions are liquid detergent compositions. In one preferred embodiment of the present invention the compositions are high active formulations such that said compositions comprise 75% to 50% by weight, preferably from 70% to 55% by weight, most preferably from 65% to 55% by weight of a liquid carrier, e.g., water, preferably a mixture of water and a C1-C4 monohydric alcohol (e.g., ethanol, propanol, isopropanol, butanol, and mixtures thereof), with ethanol being the preferred monohydric alcohol or a mixture of water and C1-C4 dihydric alcohol (e.g.: propylene glycol). In another preferred embodiment of the present invention the detergent composition may be in a concentrated form, such that the composition is diluted in water prior to usage.

EXAMPLES 1-2

The following liquid compositions of the present invention are prepared by mixing the listed ingredients in the given amounts.

<u>Ingredients:</u>	<u>Weight %</u>	
	<u>Ex. 1</u>	<u>Ex. 2</u>
C12,13E2.2Sulfate	19.2	19.2
C12,14 N,N-dimethyl amine oxide	4	4
C12,14 polyhydroxy fatty acid amide	4	4
2-butyl octanoic acid	0	2
Polymer	2	2
C9,11E9 Nonionic	2.67	2.67
Ca++ (calcium xylene sulfonate)	0.27	0.27
Mg++ (MgCl2)	0.53	0.53
Ethanol	2.2	3
DTPA	0.04	0.04
Perfume, water, minors	Balance	Balance

C12,13E2.2Sulfate = Mixed C12 and C13 alkyl ethoxy sulfate, having an average of 2.2 ethoxy units per molecule.

C12,14 polyhydroxy fatty acid amide = Mixed C12 and C14 fatty acid N-methyl glucamide.

Polymer = a suds enhancing polymer of formula  $\text{Cap} - \text{E}_n - \text{B} - \text{E}_n - \text{Cap}$  wherein  $\text{Cap} = \text{CH}_3$ ,  $n=16$ ,  $m=1.75$  and  $\text{S}=\text{PG}$  as described hereinbefore.

EXAMPLES 3-5

The following liquid compositions of the present invention are prepared by mixing the listed ingredients in the given amounts.

<u>Ingredients:</u>	<u>Weight %</u>		
	<u>Ex. 3</u>	<u>Ex. 4</u>	<u>Ex. 5</u>
C12,13E1.6Sulfate	19.6	21.2	21.2
C12,14 dimethyl amine oxide	4.1	4.4	
4.4			
C12,14 polyhydroxy fatty acid amide	4.1	4.4	
4.4			

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Polymer	1	1	1
Nonionic (CnEm) (C8E12)	6.5 (C10E8)	4 (C8E12)	4
Ca++ (calcium xylene sulfonate)	0.3	0	0
Ca++ (CaCl2) 0.2	0	0	
Mg++	0.44	0.44	0.44
Ethanol	6	6	6
DTPA	0.04	0.04	0.04
Perfume, water, minors	Balance	Balance	

C12,13E1.6Sulfate = Mixed C12 and C13 alkyl ethoxy sulfate, having an average of 1.6 ethoxy units per molecule.

C12,14 polyhydroxy fatty acid amide = Mixed C12 and C14 fatty acid N-methyl glucamide.

Polymer = a suds enhancing polymer of formula  $\text{Cap} - \text{E}_n - \text{B} - \text{E}_n - \text{Cap}$  wherein  $\text{Cap} = \text{CH}_3$ ,  $n=16$ ,  $m=1.75$  and  $\text{S}=\text{PG}$  as described hereinbefore.

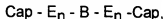


What is claimed is:

1. A liquid detergent composition comprising:

(a) greater than 3% nonionic surfactants selected from alkylpolysaccharides, polyhydroxy fatty acid amides, alkyl polyethoxylates, alkyl phenol ethoxylates and mixtures thereof; and

(b) at least 0.1% of a suds enhancing polymer having the formula:



wherein each Cap is independently selected from the group consisting of  $-\text{CH}_2\text{CH}(\text{SO}_2^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}(\text{SO}_3^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}_3$ , and  $-\text{CH}_3$ ;

at least one of the  $\text{E}_n$  is a poly(oxyethylene)oxy moiety having the formula  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_{n-1}-\text{CH}_2\text{CH}_2\text{O}-$ , wherein n is from 7 to 43; and

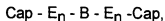
B is a polymer backbone of the formula  $(\text{T-S})_m\text{-T}$  wherein: T is a terephthaloyl moiety having the formula  $-\text{C}(\text{O})-(\text{C}_6\text{H}_4)-\text{C}(\text{O})-$ ; each S is independently selected from PG moieties having the formulas  $-\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}-$  or  $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}-$  and EG moieties having the formula  $-\text{OCH}_2\text{CH}_2\text{O}-$ ; m is within the range of from 0 to 7; and the ratio of EG:PG is less than 3:1.

2. A liquid detergent composition according to Claim 1 wherein the nonionic surfactant is selected from polyhydroxy fatty acid amides, alkyl polyethoxylates, and mixtures thereof.

3. A liquid detergent composition comprising:

(a) from 4% to 20% nonionic surfactants selected from polyhydroxy fatty acid amides, alkyl polyethoxylates, and mixtures thereof; and

(b) at least 0.2% to 3% of a suds enhancing polymer having the formula:



wherein each Cap is independently selected from the group consisting of  $-\text{CH}_2\text{CH}(\text{SO}_2^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}(\text{SO}_3^-)\text{CH}_2(\text{SO}_3^-)$ ,  $-\text{CH}_2\text{CH}_3$ , and  $-\text{CH}_3$ ;

at least one of the  $\text{E}_n$  is a poly(oxyethylene)oxy moiety having the formula  $-\text{O}(\text{CH}_2\text{CH}_2\text{O})_{n-1}-\text{CH}_2\text{CH}_2\text{O}-$ , wherein n is from 7 to 43; and

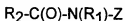
B is a polymer backbone of the formula  $(\text{T-S})_m\text{-T}$  wherein: T is a terephthaloyl moiety having the formula  $-\text{C}(\text{O})-(\text{C}_6\text{H}_4)-\text{C}(\text{O})-$ ; each S is independently selected from PG moieties having the formulas -

$\text{OCH}(\text{CH}_3)\text{CH}_2\text{O}-$  or  $-\text{OCH}_2\text{CH}(\text{CH}_3)\text{O}-$  and EG moieties having the formula  $-\text{OCH}_2\text{CH}_2\text{O}-$ ; m is within the range of from 0 to 7; and the ratio of EG:PG is less than 3:1.

4. A liquid detergent composition according to any of Claims 1-3 wherein the polymer has a ratio of EG:PG of less than 1:1.

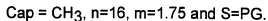
5. A liquid detergent composition according to any of Claims 1-4 comprising from 1% to 20%, preferably from 2% to 10%, of polyhydroxy fatty acid amides and from 0.5% to 10%, preferably from 1% to 5%, of alkyl polyethoxylates.

6. A liquid detergent composition according to any of Claims 1-5 comprising polyhydroxy fatty acid amides having the formula:



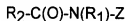
wherein  $\text{R}_1$  is H, a  $\text{C}_1\text{-C}_4$  hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or mixtures thereof;  $\text{R}_2$  is a  $\text{C}_5\text{-C}_{31}$  hydrocarbyl; and Z is a polyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyl groups directly connected to the chain or an alkoxylated derivative thereof.

7. A liquid detergent composition according to any of Claims 1-6 wherein the polymer is selected from polymers wherein:



8. A liquid detergent composition according to any of Claims 1-7 further comprising from 1% to 15% of an amine oxide or mixture of amine oxides.

9. A liquid detergent composition according to any of Claims 1-8 comprising polyhydroxy fatty acid amides having the formula:



wherein  $\text{R}_1$  is a  $\text{C}_1\text{-C}_4$  hydrocarbyl;  $\text{R}_2$  is a straight chain  $\text{C}_{11}\text{-C}_{17}$  alkyl or alkenyl or mixtures thereof; and Z is a reducing sugar selected from glucose, fructose, maltose, lactose, galactose, mannose and xylose.

## INTERNATIONAL SEARCH REPORT

 Internat. Application No  
 PCT/US 96/07447

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/37 C11D1/83 C11D3/22 C11D3/20 C11D3/32

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 576 777 (PROCTER & GAMBLE) 5 January 1994 see claims 1,5,6; example II ---	1-6,9
X	WO,A,92 17523 (PROCTER & GAMBLE) 15 October 1992 see claims 1,3; examples I,,XII ---	1-5,9
X	EP,A,0 357 280 (PROCTER & GAMBLE) 7 March 1990 see claims 1,6,8; examples 6,8 & US,A,4 968 451 cited in the application ---	1-4
A	DE,A,43 44 357 (HENKEL KGAA) 29 June 1995 see claim 1; examples; table 1 ---	1-3
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 September 1996

Date of mailing of the international search report

21. 10. 96

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentreisen 2  
 NL - 2280 HV Rijswijk  
 Tel.: (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

## INTERNATIONAL SEARCH REPORT

Internat. J. Application No.  
PCT/US 96/07447

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 221 774 (PROCTER & GAMBLE) 13 May 1987 see examples XXIII, FORM.U & US,A,5 167 872 cited in the application ---	1
A	EP,A,0 185 427 (PROCTER & GAMBLE) 25 June 1986 see claims 10,12; examples EMB,II,IV & US,A,4 702 857 cited in the application -----	1,2

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/07447

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0576777	05-01-94	AU-A-	4411193
		CA-A-	2138945
		CN-A-	1084558
		JP-T-	7508304
		WO-A-	9400546
-----			
WO-A-9217523	15-10-92	AU-A-	1753292
		CA-A-	2106217
		CN-A-	1066680
		JP-T-	6506251
		NZ-A-	242150
-----			
EP-A-0357280	07-03-90	AT-T-	134669
		AU-B-	625762
		AU-A-	4028989
		CA-A-	1332953
		DE-D-	68925765
		JP-A-	2163118
		US-A-	4968451
-----			
DE-A-4344357	29-06-95	WO-A-	9518207
-----			
EP-A-0221774	13-05-87	US-A-	4772423
		AU-B-	605114
		AU-A-	6454386
		CA-A-	1301582
		DE-A-	3685720
		IE-B-	59208
		JP-B-	7116478
		JP-A-	62181400
		US-A-	5167872
-----			
EP-A-0185427	25-06-86	AU-B-	580122
		AU-A-	5153685
		CA-A-	1315286
		DE-A-	3585505
		FI-C-	91079
		GB-A, B	2168989
		HK-A-	50394
IE-B-	58784		

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 96/07447

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0185427		JP-A- 61209299	17-09-86
		JP-A- 7166192	27-06-95
		US-A- 4861512	29-08-89
		US-A- 4702857	27-10-87
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